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## Low hydrogen content in trimethylsilane-based dielectric barriers deposited by inductively coupled plasma

Jia-Min Shieh,<sup>a)</sup> Kou-Chiang Tsai, and Bau-Tong Dai

National Nano Device Laboratories, 1001-1 Ta-Hsueh Road, Hsinchu, Taiwan 30050, Republic of China

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Dielectric barriers of trimethylsilane-based hydrogenated amorphous silicon carbide  $(a-SiC_r:H)$ for damascene metalization were synthesized by inductively coupled plasma (ICP) chemical vapor deposition methods. The high ionization efficiency from ICP, resulting in a-SiC<sub>x</sub>:H films that contain only a little hydrogen, is explored as a major mechanism that yields such a film not only with a high breakdown field of 3.7 MV/cm and a low leakage current  $<6.0\times10^{-10}$  A/cm<sup>2</sup> (at 1.0 MV/cm), but also with a low stress (-5 MPa) and high hardness (11 GPa). Additionally, the dielectric constant of the a-SiC<sub>x</sub>:H films is maintained below 4.2.  $\odot$  2002 American Institute of *Physics.* [DOI: 10.1063/1.1500794]

The integration of Cu metals and intermetal dielectrics (IMD) with a low dielectric constant (low-K) continues to dominate the interconnect schemes in the integrated circuit industry, as feature sizes are scaled down below several tens of nanometers.<sup>1</sup> A dielectric barrier against copper diffusion and an etch stop layer for patterning is normally introduced.<sup>2-6</sup> Silicon nitride (SiN) has for a long time been used as a masking and passivating layer.<sup>2</sup> Recently, a developed dielectric barrier material hydrogenated amorphous silicon carbide<sup>3-6</sup> (a-SiC<sub>r</sub>:H simplified as SiC hereinafter), which is deposited in plasma-enhanced chemical vapor deposition (PECVD) system using organosilicon<sup>3-7</sup> as a precursor, is the most promising candidate to replace SiN, because of its low dielectric constant (<5).

Furthermore, high density plasma chemical vapor deposition (HDPCVD) dielectrics<sup>8</sup> perform better than those formed by other methods, even in device applications<sup>9</sup> or IMD,<sup>2</sup> due to low interface trap density, smooth interface,<sup>9</sup> and a reduction in the number of carrier trapping sites in the films caused by the presence of less hydrogen.<sup>10</sup> The presence of only a few hydrogen-containing species in the dielectrics also increases films' hardness,11 thus increasing the etching selectivity. Nevertheless, a few studies have reported HDPCVD SiC dielectric barriers. This article reports organosilicon-based SiC films formed in an inductively coupled plasma (ICP) HDPCVD system with an excellent dielectric barrier integrity with a high breakdown field, low leakage current, and high mechanical strength.

SiC films were deposited on a 6 in.  $P^+(100)$  Si wafer in HDPCVD system using trimethylsilane the ICP  $[Si(CH_3)_3H]$  (3MS) as a precursor. For comparison, low-K carbon-doped oxide (SiOC),<sup>7</sup> SiO<sub>2</sub> films in the HDPCVD system and SiO<sub>2</sub> films in the PECVD system are deposited. Table I lists the deposition parameters for those samples. In the ICP HDPCVD system, a rf power source (13.56 MHz) is connected to the copper coil outside the ceramic plate of the upper chamber. All HDPCVD dielectrics were deposited without a rf bias power due to dielectric gap-filling not considered herein.<sup>8</sup> Fourier-transform infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectrometry were employed to characterize the silicon/carbon ratio and hydrogen concentration (atom percentage) in relation to deposition parameters.<sup>3-5</sup> The mechanical properties of films were examined using a nanoindenter (MTS, Inc.). The thermal stability was studied by curing dielectric films in a furnace for 30 min in  $N_2$  ambient, at a flow rate of 10 l/min. The current-voltage characteristics and dielectric constants of the films were evaluated using the Al-gated metal-insulatorsemiconductor (MIS) capacitors. In MIS devices, the thickness of all dielectrics was 100 nm.

Figure 1(a) indicates that the deposition rate decreases from 59 to 51 Å/s as the substrate temperature increases from 100 to 375 °C. In this case, ICP power is 500 W. The deposition rate should decline if the high temperature effect weakens the adsorption between the deposited substrate with the precursor gases.<sup>12</sup> The dielectric constant of SiC films increases from 4.0 to 4.35 with substrate temperature.

Figure 1(a) also displays Si (2P) and C (1S) XPS spectra of SiC films deposited at an ICP power of around 500 W, and process temperature of around 300 °C. By analyzing all such spectra of films in Fig. 1(a), Fig. 1(b) depicts that the silicon/carbon (Si/C) ratio in the SiC films increases by about 20% (0.83-1.05) as the substrate temperature increases from 100 to 375 °C. Katayama et al.<sup>13</sup> concluded that Si-rich SiC films have a diamond-like tetrahedral coordination while the C-rich SiC films have a graphite-like threefold coordination. Moreover, for a diamond-like SiC film, a little hydrogen remains (or fewer microvoids remain) in the films, resulting in denser films with higher dielectric constants, whereas an increase in C content introduces a more polymer-like porous structure in the SiC films with lower dielectric constants.<sup>14</sup> Referring to the deposition mechanism of amorphous SiC<sup>15</sup> and Si (a-Si)<sup>16</sup> films, the hydrogen content of the films decreases as the process temperature increases owing to the formation of a denser network by a high surface mobility of reactive species<sup>15</sup> and a lower deposition rate facilitating hydrogen outgassing.<sup>16</sup> Those phenomena can explain the process temperature dependence of the Si/C ratio and the dielec-

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<sup>&</sup>lt;sup>a)</sup>Electronic mail: jmshieh@ndl.gov.tw

TABLE I. Comparison of deposition parameters and electrical characteristics of films in this study with those of PECVD SiC films reported in Refs. 3–6. Leakage currents and breakdown fields of films measured at 1 MV/cm, and  $1.0 \times 10^{-6}$  A/cm<sup>2</sup>, respectively.

	PECVD $a$ -SiC <sub>x</sub> :H	HDPCVD a-SiC <sub>x</sub> :H	HDPCVD SiOC	HPCVD SiO <sub>2</sub>	PECVD SiO <sub>2</sub>
Si(CH <sub>3</sub> ) <sub>3</sub> H (sccm)	>100	$\sim 10$	10		
SiH <sub>4</sub> (sccm)				5	5
N <sub>2</sub> O (sccm)			100	125	125
Chamber pressure (mTorr)	$\sim$ 5000	5	5	5	$\sim 600$
Substrate temperature (°C)	$\sim$ 300	300	300	300	300
rf power (W)	$\sim 450$	500	500	300	300
Dielectric constant	<5	4.0-4.3	2.9	3.95	3.95
Leakage current (nA/cm <sup>2</sup> )	$\sim 1$	0.6	0.4	0.18	0.5
Breakdown field (MV/cm)	$\sim 2.7$	3.7	≥7	≥8	≥8

tric constant of the SiC films. Furthermore, Windischmann<sup>17</sup> proposed that impurities (hydrogen) in the a-SiC<sub>x</sub>:H films are responsible for the intrinsic compressive stress. In the case considered here, a compressive to tensile stress transition is observed as the process temperature increases, as shown in Fig. 1(b), because the dissociation of hydrogenated bonds (C–H and Si–H) induces a compressive stress relaxation and, then the formation of more Si–C bonds produces a tensile stress.

Figure 2(a) shows that an increase in the ICP power increases the deposition rate, due to an increase in the degree of dissociation of the gas. In this case, the substrate temperature is 300 °C. SiC films slowly synthesized by lower ICP power results in a denser structure with less hydrogen (higher Si/C ratio), as shown in Fig. 2(b), not only leading to SiC films with higher dielectric constants as shown in Fig. 2(a), but also inducing almost no stress in the films. According to Refs. 3-6, the ratio of silicon to carbon in the PECVD SiC films is about 1:1; and a breakdown field of 2.7 MV/cm (at  $1.0 \times 10^{-6}$  A/cm<sup>2</sup>) and a leakage current ~1.0  $\times 10^{-9}$  A/cm<sup>2</sup> (at 1.0 MV/cm) are obtained. Nevertheless, a few changes in the deposition rate and the dielectric constant of HDPCVD SiC films over the wide range of deposition conditions enables to optimize the deposits with better quali-ties than PECVD SiC films.<sup>3-6</sup> Figure 3 shows a leakage current below  $6.0 \times 10^{-10}$  A/cm<sup>2</sup> (at 1.0 MV/cm) and a breakdown voltage above 3.7 MV/cm (at  $1.0 \times 10^{-6}$  A/cm<sup>2</sup>) for the deposition of HDPCVD SiC films at the high temperature (>250 °C) and low ICP power (<500 W). In addition, Figs. 1(b) and 2(b) depict the SiC films with a low stress of around -5 MPa as compared to -50 to -150 MPa in PECVD SiC films.<sup>3,4</sup>

Comparing the electrical characteristics of dioxide films deposited by HDPCVD to those deposited by PECVD is also instructive. The flatband voltage  $V_{\rm FB}$  for PECVD dioxide of around -1.7 V decreases to that for HDPCVD dioxide of around -0.76 V. Moreover, in the same devices, the leakage current of HDPCVD dioxide is  $\sim 1.8 \times 10^{-10}$  A/cm<sup>2</sup> (at 1.0 MV/cm) and is smaller than  $\sim 5.0 \times 10^{-10}$  A/cm<sup>2</sup> for PECVD dioxide.

The improved electrical features in the HDPCVD dioxide or SiC films, as listed in Table I, are probably attributable to a low interface trap density, smooth interface and a reduction in the number of carrier trapping sites in the films caused by the presence of less hydrogen. The latter factor effect of the HDPCVD method has already been observed in many dielectrics films.<sup>2,18</sup> The hydrogen concentration in the HDPCVD SiC films is measured<sup>3–5</sup> to be in the range of 12%–20%, which is lower than in the results of Refs. 4 and 5 (25%–30% for PECVD 3MS-based SiC), and Ref. 19 (30%–40% for PECVD silane-based SiC). Consequently, the relative hardness (relative to Si(100)) and the relative Young's modulus of HDPCVD SiC films are around 95%, and 65%, respectively; both values exceed those reported (89%, 56%).<sup>4</sup>

Introducing organosilicon 3MS with N<sub>2</sub>O gas together into CVD reactions yields low-*K* SiOC films.<sup>7</sup> Figure 4(b) shows that the CH<sub>m</sub> and SiH<sub>n</sub> bonds disappear in the FTIR



FIG. 1. (a) Deposition rate and dielectric constant and (b) Si/C ratio and stress of SiC films as a function of process temperature. Si (2*P*), C (1*S*) XPS spectra of SiC films deposited at ICP power  $\sim$  500 W, process temperature  $\sim$  300 °C are also shown.

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FIG. 2. (a) Deposition rate and dielectric constant and (b) Si/C ratio and stress of SiC films as a function of ICP power.

spectra of HDPCVD low-*K* SiOC which clearly differ from the observed spectra of PECVD SiOC,<sup>7</sup> indicating that the HDPCVD approach actually reduces the formation of C–H and Si–H bonds and hydrogen content of the films. The hydrogen in PECVD SiC films is due to the incorporation of  $CH_x$  and SiH<sub>x</sub> groups, and the former is the dominant constituent.<sup>19</sup> High density plasma reactors produce a high electron temperature efficiently dissociating Si(CH<sub>3</sub>)<sub>3</sub>H precursors and then giving fewer CH<sub>3</sub> groups to the films. This mechanism leads to HDPCVD SiC films with less hydrogen than PECVD SiC films. Figure 4(a) displays FTIR spectra of HDPCVD SiC. After annealing at 550 °C for 30 min, the FTIR spectrum, dielectric constants, stresses, and leakage currents remain almost unchanged as shown in Figs. 3 and 4.

In conclusion, SiC barrier layers were deposited by a HDPCVD system. The high fractional ionization capacity in the HPDCVD system deposits films with less hydrogen than PECVD SiC films. This factor results in HDPCVD SiC films



FIG. 3. Leakage currents of SiC films before and after thermal annealing, measured using metal/SiC/Si MIS capacitors with Al gates. The inset shows the dielectric constant and stress of SiC films as functions of annealing temperature.



FIG. 4. FTIR spectra of (a) SiC films and (b) SiOC films, before and after thermal annealing at various temperatures.

with a high breakdown field, low leakage, high deposition rate, low stress, and high mechanical strength. HDPCVD SiC films remain stable at above annealing temperature of  $550 \,^{\circ}$ C.

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